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Short communication

New approach to flame retardancy using plasma assisted surface polymerisation techniques

Serge Bourbigot*, Charaffedine Jama, Michel Le Bras, R. Delobel, O. Dessaux, P. Goudmand

Laboratoire de Génie des Procédés d'Interactions Fluides Réactifs-Matériaux UPRES EA2698, ENSCL, Université des Sciences et Technologies de Lille, BP 108, 59652 Villeneuve d'Ascq Cedex, France

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Abstract

We have used a new approach to flame retard polyamide-6 using plasma assisted surface polymerisation techniques. It shows promising result because with a polysiloxane coating of about 50 μm thick on polyamide-6, the rate of heat release decreases by 30% in comparison with the virgin polyamide-6. Moreover the coating on PA-6 leads to more incomplete combustion reactions.

1. Introduction

Polymers are used in many fields such as housing materials, transport or electrical engineering applications. Due to their chemical constitution, these polymers are easily flammable and so, flame retardancy becomes an important requirement for many of them. This can be obtained by several ways such as incorporation of additives (the most classical one) [1,2], the chemical modification of the macromolecule [3] or by surface modification (γ-rays radiation) [4,5]. The first one provides good flame retardancy properties and many flame retardants are commercially available. However, the additive loading in the polymer may decrease their mechanical properties or lead to ecological problems (e.g. incineration of polymers loaded with halogenated flame retardants). The chemical modification of the polymer is generally not easy to do in the industrial scale. The third way seems to be attractive but much work remains to be done.

In this work, we investigate another route of surface modification by laying down a thin film on the polymer using plasma assisted polymerisation. Plasma enhanced chemical vapor deposition (PECVD) is one of the widely used processes for deposition of thin films. Nevertheless with the PECVD process, there is always some substrate damage induced to sensitive substrates by high energy particle bombardment from the plasma. Among the numerous varieties of plasma assisted polymerization techniques, remote PECVD (RPECVD) has recently attracted considerable interest to tackle this disadvantage. Our laboratory has developed a plasma deposition process induced by cold remote nitrogen plasma (CRNP). In this process the substrate is removed from the plasma because the plasma and the reaction chamber are spatially separated [5–10].

CRNP assisted polymerization of organosilicone compounds is an interesting preparation technique for thin polysiloxane based films. This polymer is known to have good thermal stability and flame retardancy properties of interest [11,12]. Specific industrial aspects of the CRNP process have been protected by patents [12–15].

The main reactive species of the CRNP are nitrogen atoms in the ground electronic state and nitrogen molecules electronically and vibrationally excited. The CRNP is then a non ionised reactive zone and is characterised by an important thermodynamic nonequilibrium state [16]: the translation temperature is roughly the ambient temperature but the vibrational temperature Tv depends on the pressure range (for $P = 1000$ Pa, $Tv = 2500$–3000 K).

In this work the CRNP process is used to deposit thin films on a polyamide 6 (PA-6) substrate by reaction

* Corresponding author. Tel.: +33-3-20434925.
E-mail address: serge.bourbigot@ensc-lille.fr (S. Bourbigot)

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with 1.1.3.3-tetramethyldisiloxane monomer. The flame retardancy of the coated PA-6 is then evaluated using the cone calorimeter. This paper shows the first results of the investigation.

2. Experimental

2.1. Materials

Raw materials are polyamide-6 (PA-6, as pellets supplied by Rhône Poulenc) and the monomer is 1.1.3.3-tetramethyldisiloxane 97% (TMDS) which was supplied from Aldrich Chemical Co. Sheets were then obtained using a Darragon press at 235°C with a pressure of 10^6 Pa. The size of the sample is $(2\times2\times0.3)$ cm^3. It is small because of some limitations of the laboratory CNRP apparatus.

2.2. Plasma device

Fig. 1 shows the experimental set-up of a CRNP assisted deposition reactor. Nitrogen is introduced under a pressure of 4.2 hPa at a flow rate of 1.8 slpm in a quartz tube of 33 mm outer diameter. The discharge excitation is created by a coaxial coupling device at 2450 MHz. The gas containing excited species is extracted from the discharge zone by a primary pump. The reactive gas (TMDS) is injected in the reaction chamber through a coaxial injector at a distance of 1.2 m downstream from the discharge. Such a distance avoids substrate damage induced by the charged particles. In these experimental conditions, the modified PA-6 depth may be assumed about an order of magnitude of one nanometer (formation of oxidised species).

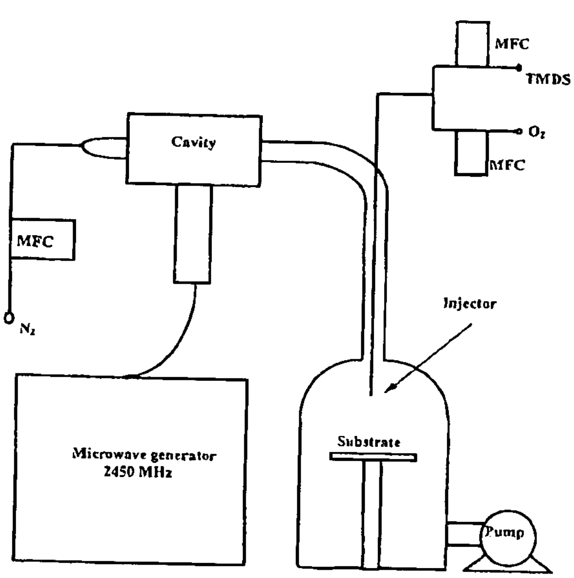

Fig. 1. Experimental set-up.

Samples are disposed horizontally in the reactor and are coated on each face (in this case, the coating is about 50 µm thick). The samples are totally coated in two steps, these two steps are separated by an open air operation. In order to obtain homogeneous deposits, the substrates are located at a distance of 10 cm from the injector inlet. The incident microwave power is maintained constant and equal to 600 W. The oxygen at flow rate of 50 sccm is mixed to a constant TMDS flow rate of 5 sccm. The deposition time is taken equal to 20 min for each face.

2.3. Cone calorimetry

Samples were exposed in a Stanton Redcroft cone calorimeter under an external heat flux of 35 kW/m^2 which represents the heat flux found in the vicinity of solid-fuel ignition source [17]. One obtained conventional data (RHR, Volume of Smoke Production (VSP), weight loss, weight loss rate,. . .) using software developed in our laboratory.

3. Results and discussion

The shape of the RHR (Rate of Heat Release) curves of the coated PA-6 and of the virgin PA-6 are similar (Fig. 2). The ignition time of the coated PA-6 (about 100 s) is lower than that one of virgin PA-6 (about 140s). However, the RHR peak of the coated PA-6 (1300 kW/m^2) is decreased by 30% in comparison with the virgin PA-6 (1850 kW/m^2). This result can be explained by defects in the coating (free radical species in the coating such as $CH_3^{\bullet}$ [6]). This may induce faster degradation during heating and then decreases the ignition time. When the ignition begins, a physical barrier is formed by the coating and the RHR values are reduced. It is confirmed by the THE (Total Heat Evolved) curves (Fig. 3) which show that the THE values are decreased by 23% (from 30 to 23 kJ). The difference of THE values can be explained by the formation of char (visual observations during the experiment).

The volume of smoke production (Fig. 4) shows that the maximum values of the polymers are quite similar. However, the VSP peak of the coated PA-6 occurs

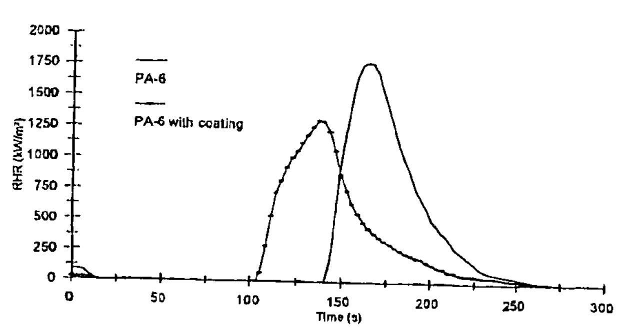

Fig. 2. RHR values versus time of virgin PA-6 and coated PA-6.

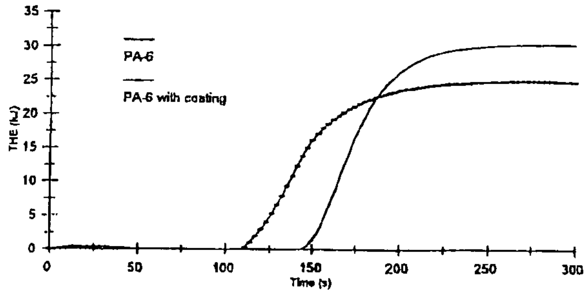

Fig. 3. THE values versus time of virgin PA-6 and coated PA-6.

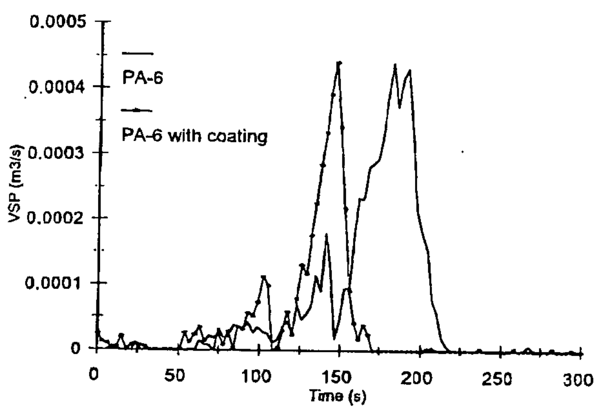

Fig. 4. Evolution of smoke production (VSP) versus time of virgin PA-6 and coated PA-6.

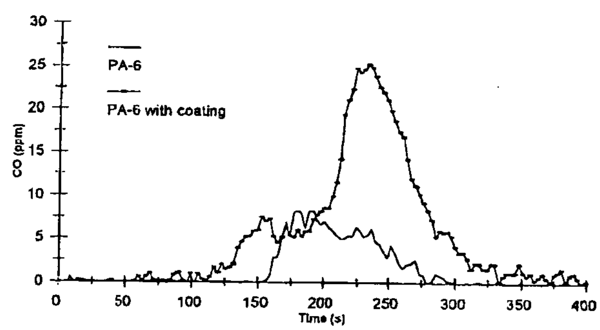

Fig. 5. Evolution of CO versus time of virgin PA-6 and coated PA-6.

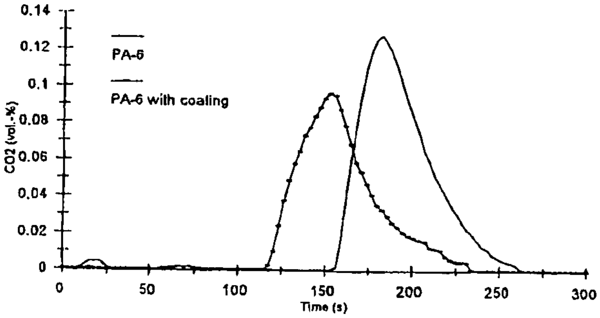

Fig. 6. Evolution of CO2 versus time of virgin PA-6 and coated PA-6.

sooner than that of the PA-6. This can be explained as above in the case of RHR curves.

The evolution of the CO and CO_2 curves show an interesting result (Figs. 5 and 6). The CO values of the coated PA-6 are very high in comparison with the virgin PA-6. In the case of the CO_2, the contrary is observed. This means that the combustion is more incomplete in the case of the coated PA-6.

4. Conclusion

In this work, we have used a new approach to flame retard polyamide-6 using plasma assisted surface polymerisation techniques. It shows promising results because with a polysiloxane coating of about 50 μm thick on PA-6, the rate of heat release decreases by 30% in comparison with the virgin PA-6. Moreover the coating on PA-6 leads to more incomplete combustion reactions.

This approach appears as very interesting because only one treatment allows one to get many different properties such as flame retardancy, damping, film deposition or hindering of additive diffusion out of the host matrix.

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